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# Molecular hydrogen (H<sub>2</sub>) combustion emissions and their isotope (D/H) signatures from domestic heaters, diesel vehicle engines, waste incinerator plants, and biomass burning

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## Abstract

Molecular hydrogen ( $H_2$ ), its stable isotope signature ( $\delta D$ ), and the key combustion parameters carbon monoxide (CO), carbon dioxide ( $CO_2$ ), and methane ( $CH_4$ ) were measured from various combustion processes.  $H_2$  in the exhaust of gas and oil-fired heaters and of waste incinerator plants was generally depleted compared to ambient intake air, while CO was significantly elevated. These findings contradict the often assumed co-occurring net  $H_2$  and CO emissions in combustion processes and suggest that previous  $H_2$  emissions from combustion may have been overestimated when scaled to CO emissions. For the heater exhausts,  $H_2$  and  $\delta D$  generally decrease with increasing fuel-to-air ratio, from ambient values of  $\sim 0.5$  ppm and  $+130$  ‰ to 0.2 ppm and  $-206$  ‰, respectively. These results are interpreted as a combination of an isotopically light  $H_2$  source from fossil fuel combustion and a D/H kinetic isotope fractionation of hydrogen in the advected ambient air during its partial removal during combustion. Diesel exhaust measurements from dynamometer test stand driving cycles show elevated  $H_2$  and CO emissions during cold-start and some acceleration phases. Their molar  $H_2/CO$  ratios are  $<0.25$ , significantly smaller than those for gasoline combustion. Using  $H_2/CO$  emission ratios, along with CO global emission inventories, we estimate global  $H_2$  emissions for 2000, 2005, and 2010. For road transportation (gasoline and diesel), we calculate  $8.6 \pm 2.1$  Tg,  $6.3 \pm 1.5$  Tg, and  $4.1 \pm 1.0$  Tg, respectively, whereas the contribution from diesel vehicles has increased from 5 % to 8 % over this time. Other fossil fuel emissions are believed to be negligible but  $H_2$  emissions from coal combustion are unknown. For residential (domestic) emissions, which are likely dominated by biofuel combustion, emissions for the same years are estimated at  $2.7 \pm 0.7$  Tg,  $2.8 \pm 0.7$  Tg, and  $3.0 \pm 0.8$  Tg, respectively. Our wood combustion measurements are combined with results from the literature to calculate biomass burning emissions. For these estimates, we propose a molar  $H_2/CH_4$  ratio of 3.3, when using  $CH_4$  emission inventories. When using this approach, our resulting global biomass burning  $H_2$  emissions agree well with published results, suggesting that  $CH_4$  emissions may be a good proxy for  $H_2$  emissions.

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## 1 Introduction

The atmospheric budget of molecular hydrogen ( $H_2$ ) has recently gained increasing interest because of the ongoing discussion of a potential shift from our fossil fuel-based energy economy, to one that is based on  $H_2$  as an energy carrier. Such a shift could lead to increased anthropogenic emissions from leakage of  $H_2$ , and therefore potentially disturb the chemistry and physics of our atmosphere (Schultz et al., 2003; Warwick et al., 2004). A better understanding of the current anthropogenic contribution to the atmospheric  $H_2$  budget is a prerequisite for an assessment of potential future human impacts on the atmospheric  $H_2$  cycle.

$H_2$  is abundant in the atmosphere at an average mole fraction of  $\sim 0.5$  ppm (in dry air, ppm =  $10^{-6}$ ) with seasonality and an inter-hemispheric gradient both driven by the source and sink patterns. The atmosphere has not shown any significant  $H_2$  trend over the past 15 yr (Grant et al., 2010b).

The atmospheric budget of  $H_2$  is characterized by several major sources and sinks (Table 1). Their estimated quantities are highly uncertain as seen in the large ranges reported in the literature (Novelli et al., 1999; Hauglustaine and Ehhalt, 2002; Sanderson et al., 2003; Rhee et al., 2006b; Price et al., 2007; Xiao et al., 2007; Ehhalt and Rohrer, 2009; Pieterse et al., 2011; Yver et al., 2011). The sources are dominated by the atmospheric photochemical production of  $H_2$  through dissociation of methane ( $CH_4$ ) and non- $CH_4$  hydrocarbons ( $30\text{--}77\text{ Tg yr}^{-1}$ ), fossil fuel combustion and other anthropogenic emissions ( $11\text{--}20\text{ Tg yr}^{-1}$ ), and biomass and biofuel burning ( $13\text{--}20\text{ Tg yr}^{-1}$ ). Microbially-induced  $H_2$  emissions from  $N_2$  fixation on land and in the oceans are estimated at  $0\text{--}6\text{ Tg yr}^{-1}$  and  $3\text{--}6\text{ Tg yr}^{-1}$ , respectively. The dominant sinks are the enzymatic removal of  $H_2$  by soil ( $55\text{--}88\text{ Tg yr}^{-1}$ ) and the atmospheric removal through reaction with OH ( $15\text{--}19\text{ Tg yr}^{-1}$ ). The atmospheric lifetime is estimated at 1.4–2 yr (Novelli et al., 1999; Simmonds et al., 2000; Rhee et al., 2006b).

The deuterium/hydrogen (D/H) ratio is a useful tool to study the atmospheric  $H_2$  budget. Due to the large mass difference of 50 % between HH and HD, the isotopic

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signatures of the sources differ largely from one another, and the sink processes show relatively strong fractionations (Table 1). Isotope studies have revealed large deuterium enrichment in the stratosphere (Rahn et al., 2003; Röckmann et al., 2003; Rhee et al., 2006a), which are a consequence of the strong isotope fractionation in H<sub>2</sub> removal and relatively D-enriched H<sub>2</sub> that is formed photochemically from CH<sub>4</sub> (Gerst and Quay, 2001; Feilberg et al., 2007; Röckmann et al., 2010b; Nilsson et al., 2007, 2010). On the other hand, surface sources emit H<sub>2</sub> that is very depleted in D (Gerst and Quay, 2001; Rahn et al., 2002b,a; Röckmann et al., 2010a; Vollmer et al., 2010; Walter et al., 2011). These findings have helped to better constrain and understand the global H<sub>2</sub> budget in combination with ground-based D/H observations and chemical-transport models (Rice et al., 2010; Batenburg et al., 2011; Pieterse et al., 2011).

Combustion of fossil fuels is believed to be the major source of anthropogenic H<sub>2</sub> emissions (e.g. Ehhalt and Rohrer, 2009). Most of the global estimates (Table 1) are derived indirectly by using emission ratios of H<sub>2</sub> to carbon monoxide (CO) and combining these with CO emission inventories. This approach is based on the assumption that both H<sub>2</sub> and CO are products of incomplete combustion and that a constant intrinsic relationship exists between the two compounds (e.g. based on the water-gas shift reaction). Recognizing that most of the anthropogenic emissions stem from road transport-based fossil fuel combustion, some studies have distinguished between vehicular and non-vehicular emissions. Novelli et al. (1999) derived transportation-based emissions of 5–20 Tg yr<sup>-1</sup> and non-vehicular emissions of 0.4–6 Tg yr<sup>-1</sup>, resulting in a global estimate of 15 ± 10 Tg yr<sup>-1</sup>. Ehhalt and Rohrer (2009) derived mean values of 8.6 Tg yr<sup>-1</sup> for traffic emissions and 2.3 Tg yr<sup>-1</sup> for non-traffic emissions, resulting in 11 ± 4 Tg yr<sup>-1</sup>. Global traffic emissions were also estimated by Vollmer et al. (2007) using multiple methods and resulted in 5–11 Tg yr<sup>-1</sup> in 2000 and decreasing to 3–5.5 Tg yr<sup>-1</sup> by 2010. Bond et al. (2011a) estimate a decrease of H<sub>2</sub> emissions from road transportation from 4.5 Tg in 2010 to 2.3 Tg in 2020. Emissions from diesel-powered vehicles are much smaller compared to gasoline-powered vehicles because of different engine technology.

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Driven by the CO ratio approach, recent studies have been conducted to better understand the  $\Delta\text{H}_2/\Delta\text{CO}$  ratios in fossil fuel combustion, where the  $\Delta$  denotes the enhancement over background expressed as mole fractions. A fleet-integrated traffic tunnel study in Switzerland revealed a mean  $\Delta\text{H}_2/\Delta\text{CO}$  of 0.48 (Vollmer et al., 2007), and a  $\Delta\text{H}_2/\Delta\text{CO}$  of 0.45 was found from samples taken close to traffic exhaust in Germany (Hammer et al., 2009). Several recent studies of atmospheric  $\text{H}_2$  and CO in Europe have also been used to derive anthropogenic urban  $\Delta\text{H}_2/\Delta\text{CO}$  (Steinbacher et al., 2007; Hammer et al., 2009; Aalto et al., 2009; Yver et al., 2009; Bond et al., 2011b; Grant et al., 2010a; Popa et al., 2011), whereas some of these studies focussed on traffic emissions by selectively analysing the periods of rush-hour traffic. In order to derive a pure emission ratio, a correction of the measured  $\Delta\text{H}_2/\Delta\text{CO}$  was proposed by Hammer et al. (2009) to remove the influence of the soil sink. The observed  $\Delta\text{H}_2/\Delta\text{CO}$  increased from 0.33–0.43 to a narrow 0.47–0.49 in those urban studies, that have applied this correction (Hammer et al., 2009; Aalto et al., 2009; Yver et al., 2009). This is in close agreement with the results from the tunnel study (Vollmer et al., 2007). However, slightly higher  $\Delta\text{H}_2/\Delta\text{CO}$  (without soil correction) have also recently been observed for the Bristol (United Kingdom) area by Grant et al. (2010a) ( $0.57 \pm 0.06$ ) and from the Cabauw tall tower in the Netherlands by Popa et al. (2011) ( $0.54 \pm 0.07$ ). In contrast to the approach by Hammer et al. (2009), Ehhalt and Rohrer (2009) assumed that the differences in lifetimes (essentially the rapid  $\text{H}_2$  removal by soil) is negligible in suburban observations, and explained the lower observed urban ratios (compared to pure traffic) by the existence of a significant non-traffic fossil fuel source with a  $\Delta\text{H}_2/\Delta\text{CO}$  of 0.2.

Many of the global estimates of  $\text{H}_2$  emissions combine biomass burning and biofuel combustion. These combined emissions were found to range between 13 and  $20 \text{Tgyr}^{-1}$  (see summary by Ehhalt and Rohrer (2009)). Price et al. (2007) distinguished between biomass ( $10.1 \text{Tgyr}^{-1}$ ) and biofuel ( $4.4 \text{Tgyr}^{-1}$ ) combustion. Of their  $15 \text{Tgyr}^{-1}$   $\text{H}_2$  emissions from biomass burning, Ehhalt and Rohrer (2009) assigned  $4.8 \text{Tgyr}^{-1}$  to biofuel. Biomass burning emissions (excluding biofuel) are also

estimated by Yver et al. (2011) at  $7.8 \text{ Tg yr}^{-1}$  for mid-2006 to mid-2009.  $\text{H}_2$  emissions from biomass burning are also given by the Global Fire Emissions Database version 3 (GFED3, data set at <http://www.globalfiredata.org/>, see also Giglio et al. (2010) and Van der Werf et al. (2010)). These estimates were made for 1997 to 2010 ranging  
5  $5.3\text{--}12.6 \text{ Tg yr}^{-1}$  with a mean of  $7.8 \text{ Tg yr}^{-1}$ . Various methods are used in the literature to derive the emissions for biomass and biofuel burning, including the scaling of  $\text{H}_2$  to the amount of biomass burnt, to  $\text{CO}$  or  $\text{CO}_2$ , or using an isotope budget analysis (see Ehhalt and Rohrer (2009) for a summary). The  $\text{H}_2/\text{CO}$  from biomass burning has persistently been found to be lower compared to traffic combustion. Biomass burning field  
10 studies typically show  $\Delta\text{H}_2/\Delta\text{CO}$  of  $0.15\text{--}0.4$  with the majority of the published data in the narrow range of  $0.2\text{--}0.3$  (Crutzen et al., 1979; Cofer III et al., 1989, 1990, 1996; Laursen et al., 1992). Also, a recent study of controlled wood burning has shown a  $\Delta\text{H}_2/\Delta\text{CO}$  of  $0.16 \pm 0.13$  (Röckmann et al., 2010a).

The present study aims to improve our understanding of the anthropogenic  $\text{H}_2$  emissions and their isotopic signature. We have experimentally investigated various potential anthropogenic  $\text{H}_2$  sources. To our knowledge, these are the first published measurements of  $\text{H}_2$  in the exhaust of residential heaters and waste incinerator plants. A revision of the global  $\text{H}_2$  emissions from combustion is suggested, including fossil fuel, biofuel, and biomass combustion. For the latter, we use  $\text{H}_2/\text{CO}$  with updated biomass  
15 burning  $\text{CO}$  emissions and compare this approach with a new one based on  $\text{H}_2/\text{CH}_4$ . Finally, temporal changes in these emissions are addressed, a topic that has so far received little attention in the literature.

## 2 Methods

### 2.1 Residential fossil fuel and wood heater

25 Exhaust samples from residential oil, gas, and wood burners were collected in December 2008 and January 2009 in Switzerland from 9 roof-top chimneys and exhaust pipes

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(see Supplement for more details on the sampling and analysis). With the exception of the open wood fire, all heater systems are designed to heat a water reservoir of a closed-water cycle that distributes the heat through the buildings by means of hot water radiators or hot water floor heating systems. The samples were drawn through PFA tubing and transferred into 2 l glass flasks (NORMAG, Illmenau, Germany), fitted with 2 stopcocks, by means of a membrane pump (model N86-KTE, KNF Neuberger, Switzerland) to pressures of 1.8 bar. A drying cartridge containing magnesium perchlorate ( $\text{Mg}(\text{ClO}_4)_2$ ) was fitted downstream of the pump to remove  $\text{H}_2\text{O}$  from the samples in order to avoid isotopic exchange between  $\text{H}_2$  and  $\text{H}_2\text{O}$  during storage of the samples. The samples were stored in the dark and at room temperature before analysis on various instruments.

The samples were taken from a large variety of burner types, fuel systems, and burning capacities. For each location, two samples (A and B) were taken typically ~5 min apart. The sample pairs S-1 and S-2 (Table 2) were taken from oil burners of single-family houses. A variety of natural gas burners were also sampled (S-3 to S-7) ranging from single-family houses to larger building complexes. In addition to the fossil fuel-based heating systems, two wood-burning systems were also sampled. The samples S-8 were taken from a modern (2007) fully automated wood-pellet burning system of a 2-family house. The samples S-9 were taken from an indoor open fire place of a single family house, in which pieces of local beech were burnt. The samples were drawn through an opening in the chimney system ~4 m above the fire. Finally, ambient air samples were also collected during this campaign in order to determine approximate mole fractions of the air drawn for the combustion.

The samples were measured at Empa for  $\text{H}_2$  and CO in February 2009, using a gas-chromatograph (GC) with a reduction gas analyzer (RGA-3, Trace Analytical) based on mercuric oxide (HgO) reduction and UV light absorption by mercury (Vollmer et al., 2007; Bond et al., 2011b). The instrument is controlled through software for air monitoring (GCWerks, USA) and includes a correction for nonlinear system behavior (Vollmer et al., 2007; Bond et al., 2011b). The measurements of flask samples were bracketed

by the analysis of a working standard that allowed quantification and short-term instrumental drift correction. This working standard was referenced against the Max Planck Institute (MPI)-2009 primary calibration scale for H<sub>2</sub> (Jordan and Steinberg, 2011). The CO measurements were linked in a similar way to the NOAA/ESRL WMO-2000 calibration scale for CO. The mean measurement precisions were 0.6 % for H<sub>2</sub> and 0.4 % for CO (as determined from repeated analyses). The overall accuracies, including calibration scale and nonlinearity uncertainties, are estimated at ~2 %. Some of the samples' H<sub>2</sub> and/or CO exceeded the detector's response or the range characterized for nonlinear system behavior. These samples were diluted using synthetic air, from which traces of H<sub>2</sub> and CO were removed using a catalyst (Sofnocat 514, Molecular Products, Thaxted, UK).

The samples were also analyzed (May 2009) on a GC (Agilent Technologies 6890N and controlled through GCWerks) equipped with a flame-ionization detector (FID) for CO and CH<sub>4</sub>. This instrument has linear detector response in the ambient mole fraction range as found through earlier experiments (Steinbacher and Vollmer, unpublished data). For the present work, measurements of two high mole fraction standards (2.01 ppm and 8.25 ppm, traced back to NIST SRM (Standard Reference Material) 2612a) revealed a slight CO nonlinearity at higher mole fractions, which was corrected. The measurement precisions were 0.2 % for CH<sub>4</sub> and 1.1 % for CO. CO measurements are reported on the WMO-2000 calibration scale (with NIST and WMO-2000 in very close agreement, Zellweger et al., 2009) and CH<sub>4</sub> measurements are reported on the NOAA-2004 calibration scale (Dlugokencky et al., 2005). The overall accuracies, including calibration scale and nonlinearity uncertainties, are estimated at ~2 % for both compounds.

In order to quantify CO<sub>2</sub> in the exhaust samples, most samples were also analyzed by Fourier Transform Infrared (FTIR) spectroscopy applying a spectrometer (Nicolet Avatar 370 InSb, Thermo Nicolet Corp., USA) equipped with a heated (40 °C) low-volume (50 ml) flow-through gas cell with 1m path-length (Model LFT-210, Axiom Analytical Inc., USA). Infrared spectra with 0.5 cm<sup>-1</sup> optical resolution were recorded

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integrating over 128 spectral scans and trace gas mole fractions were retrieved by classical least square fitting in selected wavelength regions (Mohn et al., 2008). Calibration spectra were recorded under identical instrumental and spectroscopic conditions from certified and diluted calibration gases or by continuous injection of liquids into nitrogen.

5 The expanded standard uncertainty ( $1\sigma$ ) for  $\text{CO}_2$ ,  $\text{CO}$ , and  $\text{CH}_4$  is  $\sim 5\%$ .

$\text{H}_2$  mole fractions and stable isotope D/H analysis of  $\text{H}_2$  were conducted in March 2009 at the isotope laboratory of the Institute for Marine and Atmospheric research Utrecht (IMAU), Utrecht University, using isotope ratio mass spectrometry (Rhee et al., 2004). We report the isotope measurements using the “delta” notation,  
10  $\delta\text{D} = [(D/H)_s / (D/H)_{\text{VSMOW}} - 1] \times 1000\text{‰}$ , where s refers to the sample and VSMOW is Vienna Standard Mean Ocean Water used as reference (Craig, 1961; Gonfiantini, 1978). The mean absolute  $1\text{-}\sigma$  precision is estimated at  $4.5\text{‰}$  (Batenburg et al., 2011).

As described in the previous paragraphs,  $\text{H}_2$ ,  $\text{CO}$ , and  $\text{CH}_4$  were measured on several instruments. For those measurements that qualified for a comparison (within non-linearity ranges, well above detection limits), we found an agreement within a few per-  
15 cent for the various measurement techniques, even though many results were slightly outside the combined ( $1\sigma$ ) measurement precisions. For the final values used in our analysis, we have selected measurements from individual instruments or averages from two or more instruments. The selection was mainly based on choosing the measurements within the well-characterized nonlinearity ranges (RGA-3) and by excluding some low-mole-fraction  $\text{CH}_4$  FTIR measurements for which more uncertainty was expected.

## 2.2 Waste incinerators

Exhaust gas was sampled at six Waste incinerator facilities throughout Switzerland.  
25 These incinerators are typically designed for the combustion of household and industrial waste on a regional scale (equipped with one to four boilers and yearly waste throughput of 90 000–220 000 t) and are equipped with a sequence of filter systems to remove most particles and toxic substances. The incinerators I-1 and I-2 were sampled

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in 2008. A large set of incinerators was sampled from September 2010 to March 2011 by collection of integrated (1 week) dried (MD-070-24S-4, Perma Pure, USA) exhaust gas samples in Cali-5-Bond™ sampling bags (GSB-P/44, Ritter Apparatebau, Germany). Some of these Tedlar bag samples were cryogenically transferred ( $>0.6 \text{ l min}^{-1}$ ) into evacuated stainless steel flasks and subsequently measured on the RGA-3 a few days after transfer. Samples with CO mole fractions above 1.5 ppm were transferred directly from the Tedlar bags into a small (50 ml) stainless steel container, immediately diluted with purified ( $\text{H}_2$  and CO free) synthetic air, and subsequently analyzed on the RGA-3. CO,  $\text{CO}_2$ , and  $\text{CH}_4$  were additionally analysed by FTIR spectroscopy.

The incinerator exhaust gas samples were stored in Tedlar bags less than two weeks before transfer and/or analysis. In order to assess potential diffusive exchange/loss of  $\text{H}_2$  through the Tedlar bags during storage, a stability experiment was conducted that demonstrated sufficient storage stability over the course of our storage period, but showed significant enhancement of  $\text{H}_2$  and CO over a longer storage period (see Supplement).

### 2.3 Diesel-powered vehicles

Exhaust gas analysis from diesel-powered vehicles was conducted at Empa in 2008 as part of an extensive dynamometer test stand emission study that included  $\text{H}_2$  emissions, and that were part of a larger fleet study also including gasoline vehicles (Bond et al., 2010). This included the measurements of 5 light-duty diesel delivery vehicles and 1 diesel passenger car, most of which were tested under 6 different driving cycles. All diesel vehicles were classified by the Euro-4 emission standards. All vehicles were equipped with oxidation catalysts and three had diesel particle filters. On-line direct exhaust measurements were conducted for a suite of compounds.  $\text{H}_2$  was measured using an on-line mass spectrometer (H-sense, V&F Analyse- und Messtechnik GmbH, Austria, see Bond et al. (2010) for a description of the instrument) and CO was measured using Mexa 7100 AIA-721A and AIA-722 instruments (Horiba, Japan). The data used here are from the periods of large  $\text{H}_2$  and CO mole fractions (up to

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several hundred ppm), which occurred during all cold starts and during some of the acceleration phases. Hence our results are based on periods of emissions selected for their high emissions and they include the investigation of the H<sub>2</sub>/CO ratios, while the study by Bond et al. (2010) focused on the emissions factors covering the entire driving cycles and did not include the H<sub>2</sub>/CO ratio of diesel exhaust.

### 3 Results and discussion

#### 3.1 H<sub>2</sub> and H<sub>2</sub>/CO

In this paper, we will exclusively use the molar H<sub>2</sub>/CO ratio and not the weight-based ratio, which is sometimes used in the literature (to convert from weight-based to molar, multiply by 14). Also, we will distinguish between the ratio based on measured mole fractions, here termed “absolute ratio”, and the ratio calculated after subtraction of the background mole fraction, which are typically found in the combustion intake air (H<sub>2</sub> ≈ 0.5 ppm and CO ≈ 0.2 ppm). We express the ratio for background corrected values in the Delta (Δ) notation (ΔH<sub>2</sub>/ΔCO). This distinction is important for the discussion of the many low-mole-fraction measurements in the present study, but becomes negligible for high-mole-fraction source signals, when it is sometimes ignored in the following text. Analogously, we proceed with the molar ratio of H<sub>2</sub>/CH<sub>4</sub> and ΔH<sub>2</sub>/ΔCH<sub>4</sub>, and use CH<sub>4</sub> ≈ 1.8 ppm as a typical background mole fraction.

##### 3.1.1 Residential fossil fuel heater

Our results are shown in Fig. 1 and listed in Table 2. Most of the heater exhaust samples (S-1 to S-6) exhibit surprisingly low H<sub>2</sub> mole fractions (in dry air) in the range 0.19–0.64 ppm (parts-per-million, 10<sup>-6</sup>), which is at or below the mole fractions of the ambient intake air (~0.5 ppm). Thus many of the sampled heaters are net sinks for H<sub>2</sub>. In contrast, most heater samples have significantly elevated CO mole fractions

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(1–15 ppm) compared to the measured ambient air (0.2–0.3 ppm). Consequently, the absolute  $H_2/CO$  is small (Table 3), typically 0.05–0.2, even zero or negative when using the  $\Delta$  notation (differences to background). As an exception,  $H_2$  was significantly elevated in S-7 (3.5 ppm), a natural gas-fueled residential heater. For this heater, CO and  $CH_4$  were also largely elevated (Table 2), suggesting that the burner of this heater may not have been adjusted properly.

### 3.1.2 Residential wood heater

In contrast to the oil and gas heater exhausts, both  $H_2$  and CO are strongly elevated in the wood-based combustion samples, S-8, and S-9, with the highest  $H_2$  mole fractions for the open wood fire place (S-9B, 390 ppm) during fast burning under a strong intake air draft. For the wood pellet heater,  $H_2$  decreases from the starting phase of the burning (S-8A, 20.6 ppm) to the optimal burning phase (S-8B, 6.2 ppm) with similar air to fuel ratio for these two samples, as indicated by similar  $CO_2$  mole fractions (Fig. 2). If we generally use  $CO_2$  as a proxy for combusted fuel, then our results indicate that modern wood pellet combustion systems reduce  $H_2$  and CO emissions compared to less controlled open fires, but that they are still much larger than oil and natural gas-fueled combustion systems.

### 3.1.3 Waste incinerators

Exhaust gas mole fractions from waste incinerators were generally low, with near ambient  $H_2$  mole fractions (0.3–0.9 ppm) and enhanced CO mole fractions (3–13 ppm). This results in the absolute  $H_2/CO$  of typically 0.05–0.1 (Table 3) and virtually zero or negative in the  $\Delta$  notation (Fig. 1). Given that the sampled waste incinerators are equipped with a suite of sequential filter systems including electrostatic filters and flue gas scrubbers, the observed  $H_2$  and CO probably represent a strongly altered combustion signal. There are a few exceptions to the low- $H_2$  emissions. At plant I-2 much higher mole fractions of  $H_2$  (~2 ppm) and CO (~30 ppm) were observed, which are

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likely a result of a poor tuning of a post-filter heater (using natural gas as fuel) for NO<sub>x</sub> removal that this plant included at the time of the sampling. Additionally at three waste incinerators, individual weekly-integrated exhaust gas samples (I-4A, I-5B, I-8C) exhibited elevated H<sub>2</sub> (~4.8 ppm) and CO (~10 ppm), two of the samples also showed enhanced CH<sub>4</sub> (~1.2 ppm) compared to all other plants (<0.5 ppm).

### 3.1.4 Diesel-powered vehicles

The dynamometer test stand online diesel exhaust measurement results shown in Fig. 1 are from the study of Bond et al. (2010), but limited to episodes selected for high H<sub>2</sub> and CO emissions. We find H<sub>2</sub>/CO < 0.25 (Table 3). The ratios at ~0.01 are mainly those from the cold starts of the delivery vehicles while the ratios ~0.2 are those from high emission episodes during accelerations (but while engine and catalytic converter were hot) and from most cycles run with a passenger vehicle.

The H<sub>2</sub>/CO ratios observed for the diesel-powered vehicles are significantly smaller compared to that for gasoline-powered vehicles of 0.48 ± 0.12 found during a tunnel study (derived from the total fleet ratios by Vollmer et al., 2007) and of 1.0 (sub-cycle means of 0.48–5.7) determined from a laboratory study on vehicles using exclusively modern combustion and exhaust treatment technology (Bond et al., 2010). Hence not only are the CO emissions from diesel powered engines smaller compared to gasoline powered engines, but also the H<sub>2</sub>/CO ratios, suggesting that the global H<sub>2</sub> emissions from traffic are even more dominated by the gasoline-powered vehicles than the CO emissions.

The lower H<sub>2</sub> and CO emissions and the lower H<sub>2</sub>/CO for diesel exhaust compared to that of gasoline are most likely related to the different types of combustion. In a modern gasoline engine, the air-fuel ratio (expressed as λ) is set to near 1, where λ < 1 is fuel-rich (excess fuel) and λ > 1 is fuel-lean (excess oxygen). Under these conditions, the H<sub>2</sub> and CO are presumably strongly controlled by the the water-gas shift reaction, CO + H<sub>2</sub>O ↔ CO<sub>2</sub> + H<sub>2</sub>, and rapid isotopic exchange between H<sub>2</sub>O and H<sub>2</sub> (Vollmer et al., 2010). In contrast, diesel is combusted at higher temperatures under fuel-lean

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conditions. It is likely that the oxidation of  $H_2$  and  $CO$  by  $O_2$  becomes an important sink for these two compounds, presumably with preferential removal of  $H_2$  over  $CO$  thereby leading to the relatively low absolute  $H_2/CO$ .

### 3.2 Relationship of $\delta D$ and $H_2$ to $CO_2$

5 The isotopic signatures D/H of the heater exhaust samples were generally found to be strongly depleted (Table 2), down to  $\delta D = -206\text{‰}$ , compared to ambient air levels ( $\delta D \approx +130\text{‰}$ ). These isotopic signatures and the  $H_2$  mole fractions vs.  $CO_2$  are shown in Fig. 2, along with the measurements from the waste incinerator exhaust samples. The  $\delta D$  and the  $H_2$  mole fractions for the gas and oil heater samples both decrease  
10 with increasing fuel-air ratio, represented by increasing  $CO_2$  mole fractions. These results are difficult to interpret. At first glance, the decreasing  $H_2$  mole fractions suggest that some of the  $H_2$  in the intake air is removed during the combustion with increasing fuel-air ratio. Interestingly, if we extrapolate the linear fit in Fig. 2 to the maximum possible  $CO_2$  mole fractions of 21 % (all oxygen consumed), then the  $H_2$  equals virtually  
15 zero ( $-0.002$  ppm). However, if such a removal process was associated with a normal (positive) kinetic isotope effect (KIE), as most chemical reactions are, then the  $\delta D$  of the remaining  $H_2$  should increase. However, the opposite is observed with a strong depletion (reaching  $-325\text{‰}$  if also linearly extrapolated to 21 %  $CO_2$ ). Only an inverse KIE could explain these observations. Inverse KIEs have been observed for catalyzed  
20 reactions involving hydrogen and carbon (e.g. Shi and Jin, 2011) but we were unable to find data on the KIE of  $H_2$  combustion. Alternatively, the observed strongly-depleted D/H could mainly manifest the D/H in the fuel (oil and natural gas generally contain strongly depleted D/H, see e.g. Schimmelmann et al., 2006). However, if the hydrogen in the fuel was a significant source (and if there were no sink), then the  $H_2$  mole fraction  
25 should increase with increasing  $CO_2$  (i.e. with increasing amount of combusted fuel), which we do not observe. In such a one-source end-member system, the data would then also describe a linear relationship of  $\delta D$  vs. inverse  $H_2$  mole fraction in a “Keeling plot” as shown in Fig. 3, and point to a specific end-member isotopic signature (at

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$1/H_2 = 0$ ), which is not the case for our samples. This leads us to suggest that the results from our measurements of heater exhausts could be explained by either removal with an inverse KIE or concurrent production and removal processes – a source of  $H_2$  with significantly depleted D/H (typical combustion) and a simultaneous removal of  $H_2$  with a positive fractionation, which is, however, not large enough to compensate for the depleted D/H source.

The samples from wood fires show no obvious relationship between  $\delta D$  and  $CO_2$  (Fig. 2) but generally their  $\delta D$  values are lower than those of the oil and gas burner samples. They show relatively high combustion efficiency (low molar ( $ppm\ ppm^{-1}$ )  $CO/CO_2$  ratio, range  $8 \times 10^{-4}$ –0.12) compared to other wood combustion results by Röckmann et al. (2010a), whereas some of our samples show relatively “heavy”  $\delta D$  (Fig. 3) compared to that study. Some of the waste incinerator samples (I-1) show the lowest  $\delta D$  observed during our study (–229 to –357‰) and low  $H_2$  mole fractions resulting in very different signatures in the “Keeling plot” (Fig. 3) compared to other combustion samples. By contrast, the incinerator results from I-2, where a post-filter natural gas burner was installed, agree well with the  $1/H_2$  vs.  $\delta D$  results of other combustion processes (Fig. 3).

### 3.3 $H_2/CH_4$ from heaters, incinerators, and biomass burning

Our measurements of  $CH_4$  in the different exhausts show highly variable mole fractions (Fig. 4). While the wood combustion samples exhibit mole fractions of up to 100 ppm, the heater samples and the waste incinerator samples show much lower mole fractions, and many of these are below the ambient air mole fractions of  $\approx 2$  ppm. These combustion processes are thus a net sink of  $CH_4$ . Wood combustion and waste incinerator samples have molar  $H_2/CH_4$  ranging approximately 1–4. In contrast, most fossil fuel heater samples show ratios  $< 1$ . In Fig. 4 we also show  $H_2/CH_4$  from a variety of wildfires (savanna, boreal forests, wetlands) and burning types (smoldering and flaming) from Cofer III et al. (1989, 1990, 1996). These can be approximated by a  $\Delta H_2/\Delta CH_4 = 3.3$  (Table 3) corresponding to a weight-based ratio of 0.413. The ratios

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from our high-mole-fractions wood fire exhaust (2.4 and 3.9) bracket this ratio with reasonable agreement.

### 3.4 Implications on global H<sub>2</sub> emissions from combustion

Global H<sub>2</sub> emissions from combustion can be estimated directly by using H<sub>2</sub> emission factors, which are related to the combusted material (e.g. dry-weight or carbon content), or by using combustion ratios to other trace gases (e.g. CO), and using their corresponding emission inventories. For H<sub>2</sub>, our understanding of both approaches is currently incomplete. Our goal is to improve our understanding of the H<sub>2</sub>/CO ratio approach (Table 3) and introduce the H<sub>2</sub>/CH<sub>4</sub> approach. We estimate H<sub>2</sub> emissions from transportation, residential combustion (fossil fuel and biofuel), and biomass burning (Table 3). To deduce global emissions from H<sub>2</sub> combustion, we base our analysis mainly on the inventories by Fulton and Eads (2004), by the Emission Database For Global Atmospheric Research (EDGARv4.2) project (Olivier et al., 2002), and by GFED3. The EDGAR emission inventories are presumably based on the United Nations Framework Convention on Climate Change (UNFCCC) common reporting format (CRF) emission inventory – however, these lack emission information from many countries not reporting to UNFCCC.

#### 3.4.1 Transportation emissions

Road transport CO emissions have been undergoing large declines in recent decades (Fulton and Eads, 2004) due to improved combustion and catalytic converter technology. Fulton and Eads (2004) estimate total (gasoline and diesel) global road traffic CO emissions to decline from 270 Tg in 2000, to 200 Tg, 135 Tg, and 90 Tg in 2005, 2010, and 2015, respectively. While the road diesel CO contribution was reported very small in the 1980s (6 Tg yr<sup>-1</sup> vs. 232 Tg yr<sup>-1</sup> for gasoline, Duncan et al., 2007), the 2000s seem to show a less pronounced imbalance for these two fuel types. Fulton and Eads (2004) estimate road traffic diesel CO emissions for the above-mentioned 4 yr at

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~40 Tg, 35 Tg, 30 Tg, and 25 Tg, respectively (sum of only freight trucks and buses). Thus the relative contribution of CO emissions from diesel is steadily increasing, despite a marginally changing relative usage of the two fuel types, which are consumed in similar quantities (gasoline of  $1.13 \times 10^{12}$  vs. diesel of  $0.87 \times 10^{12}$  l gasoline-equ. for 2010, Fulton and Eads, 2004). These changes are likely caused by the large improvements in gasoline combustion clean-up technologies. For H<sub>2</sub> traffic emissions, we use the above estimates by Fulton and Eads (2004) and combining these with approximated H<sub>2</sub>/CO ratios of  $0.5 \pm 0.12$  for gasoline and  $0.15 \pm 0.1$  for diesel (Table 3). The differences of the estimates by Fulton and Eads (2004) to those by EDGAR (sector 1A3b, 206 Tg for 2000 and 155 Tg for 2005) suggests that there are large uncertainties in the CO emissions, thus we assign an error of 25 % to the Fulton and Eads (2004) uncertainties. Results for the years 2000, 2005, and 2010 are given in Table 3 and show declining traffic H<sub>2</sub> emissions and increasing relative contributions from diesel. Our traffic emission estimates are in agreement with those derived by Vollmer et al. (2007) and Bond et al. (2011a).

Our estimates are based on temporally constant H<sub>2</sub>/CO. However, a recent study by Bond et al. (2010) suggests that the average H<sub>2</sub>/CO could increase significantly with improved clean-up technologies (possibly to H<sub>2</sub>/CO  $\approx$  1). Thus it is possible that the global H<sub>2</sub> emissions from traffic may not decline as much as predicted here and by Vollmer et al. (2007), as declining CO and increasing H<sub>2</sub>/CO have some compensatory effects. We have neglected this in our estimates and have assumed that these potentially larger H<sub>2</sub>/CO are not significantly penetrating the “world” fleet so soon, and also argue that their overall CO contributions are less because these emissions with potentially enhanced H<sub>2</sub>/CO are from vehicles with reduced overall H<sub>2</sub> and CO emissions.

Diesel H<sub>2</sub> emissions are also expected to occur from diesel fuel use in water and rail transportation. According to Fulton and Eads (2004), the fuel use for these categories are roughly the same as for the sum of freight trucks and buses. Assuming the same H<sub>2</sub>/CO as for the road diesel emissions, we estimate the H<sub>2</sub> emissions from ship and rail diesel usage to equal that from road diesel vehicles (Table 3). Ultimately,

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H<sub>2</sub> emissions are also expected to occur from diesel combustion for other purposes (e.g. power generation), but these are excluded here.

### 3.4.2 Domestic emissions (biofuel and fossil fuel)

The EDGAR CO inventory has one single highly-aggregated category “Residential and others” (1A4), which contains both emissions from fossil fuel (oil, gas, coal) and biofuel. This makes it impossible to identify the component that is solely due to oil and gas emissions. The UNFCCC CRF divide their category 1A4 (“other sectors”) into 3 sub-categories, where 1A4b (“residential”) CO emissions comprise the largest fraction of 1A4. By comparing the EDGAR and UNFCCC emissions with the study by Yevich and Logan (2003) on biofuel emissions, we conclude that the dominant fraction of residential CO emissions in the developing world is from biofuel. Surprisingly, in industrialized countries, biofuel CO emissions may also play an important role compared to other emissions in the 1A4 category, even though in these countries, a large fraction of the residential energy usage derives from fossil fuel heating systems, particularly in colder climate regions. The difficulty in extracting the various subtypes of emitters in this category 1A4b is that most national emission inventories do not report on this level of detail. For Switzerland for example, residential 1A4b emissions of CO are 45 kt yr<sup>-1</sup>. However, the largest fraction (~80 %) of these CO emissions derives from biofuel (wood) burning (for heating) and from seemingly minor applications (~8 %), such as gardening tools (2-stroke engines) with very large CO emission factors. The oil and gas heating systems’ CO emissions for Switzerland are comparably small (~5 %), despite their dominance from an energy perspective. While such disaggregated emissions are not available within the publicly available UNFCCC CRF and EDGAR inventories, it supports our conclusion that on a global basis, the majority of the CO emissions from the “residential” sector are from biofuel combustion. On the basis of this finding, we adopt the biomass burning  $\Delta\text{H}_2/\Delta\text{CO}$  of  $0.25 \pm 0.05$  (Table 3) to calculate these “residential” emissions, which we derive from the literature (see Introduction). H<sub>2</sub> emissions from oil and gas are likely insignificant given the near zero  $\Delta\text{H}_2/\Delta\text{CO}$  emission ratios. CO

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emissions from residential coal combustion are likely to be small compared to biofuel emissions (the biofuel CO emissions by Yevich and Logan (2003) nearly match the total “residential” emissions in EDGAR). However, here we assume that the corresponding H<sub>2</sub> emissions are also small, i.e. that the H<sub>2</sub>/CO ratio of coal combustion is not significantly larger than that of biomass combustion. The EDGAR global estimates for domestic CO emissions show a trend of increasing emissions with time, but with relatively little temporal variation, with a mean value of 153 ± 5 Tg for 1980–2008 (Fig. 5 and Table 3). These convert to global H<sub>2</sub> emissions of 2.7 ± 0.09 Tg. Here we omit using EDGAR CH<sub>4</sub> to derive H<sub>2</sub> emissions because in this sector, fugitive CH<sub>4</sub> emissions, presumably from leakage (with presumably insignificant corresponding H<sub>2</sub> emissions), contribute strongly to the total CH<sub>4</sub> emissions of this sector. Our estimated emissions for this sector are smaller (but probably within the combined uncertainties) compared to the 4.4 Tgyr<sup>-1</sup> for biofuel by Price et al. (2007) and the 4.8 Tgyr<sup>-1</sup> by Ehhalt and Rohrer (2009) for unspecified years.

### 3.4.3 Biomass burning

For biomass burning, a 14-yr long H<sub>2</sub> emission record is available from GFED3, showing considerable temporal variability (Fig. 5). Here we test our conversions from the EDGAR and GFED3 CO and CH<sub>4</sub> emission inventories to H<sub>2</sub> emissions using the earlier discussed molar ratios of 0.25 for H<sub>2</sub>/CO and 3.3 for H<sub>2</sub>/CH<sub>4</sub>. The comparison of the GFED3 CH<sub>4</sub>-derived H<sub>2</sub> emissions compared to its H<sub>2</sub> emissions show a generally good agreement and is to some degree a confirmation of using CH<sub>4</sub> as a proxy for H<sub>2</sub> in biomass combustion processes (Fig. 5). However, there is also some degree of circular conclusion in this comparison because some of the data (e.g. Cofer III et al., 1989, 1990, 1996), which we have used in our derivation of H<sub>2</sub>/CH<sub>4</sub> are also indirectly used in GFED3 (Van der Werf et al., 2010) through the analysis of emission factors (Andreae and Merlet (2001) and updates), which partially draw on the same original emission measurements. The CO-derived H<sub>2</sub> emissions are generally lower compared to the CH<sub>4</sub>-derived H<sub>2</sub> emissions for both GFED3 and EDGAR data sets. Where common

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records are available, the EDGAR CO and CH<sub>4</sub> emissions are considerably larger (30 to 40 %) than the respective GFED3 emissions, as are consequently the corresponding H<sub>2</sub> emissions. This discrepancy may possibly be caused by EDGAR adopting older GFED version 2 values, which are significantly higher than GFED3.

5 The GFED3 biomass burning H<sub>2</sub> emission estimates are significantly lower (except for the record year 1997) compared to the global H<sub>2</sub> emissions estimate from biomass burning by Laursen et al. (1992) of 21 Tg for an unspecified year. Our molar H<sub>2</sub>/CH<sub>4</sub> ratio of 3.3 is also smaller compared to their ratio of 4.3, which we calculate from their H<sub>2</sub> and CH<sub>4</sub> emission estimates.

10 The scaling of H<sub>2</sub> emissions to the CO emissions has been performed in earlier studies with somewhat different ratios and CO emission inventories but yielding similar results, e.g. the study by Price et al. (2007). To our knowledge, this is the first time that H<sub>2</sub> emissions are scaled to CH<sub>4</sub> emissions using H<sub>2</sub>/CH<sub>4</sub> ratios.

15 The combined emissions from biomass and biofuel H<sub>2</sub> combustion are at the lower end of the range found in the literature (Table 1), and the combined estimate of  $8.4 \pm 1.6$  Tg from 2000 is the lowest ever reported for this category.

## 4 Conclusions

20 Our study has attempted to fill some of the gaps in the knowledge of H<sub>2</sub> emissions quantification from fossil fuel and biomass combustion. The low H<sub>2</sub>/CO from residential combustion processes should lead to a total urban H<sub>2</sub>/CO ratio lower than the traffic related one. This “dilution” effect would presumably be seasonal, as heating systems are more strongly used during winter time. Thus, such an effect should be seen in multi-annual urban data records if CO emissions from heating are of similar magnitude as those from traffic. Even though there is confirmatory indication in the literature  
25 (Hammer et al., 2009; Aalto et al., 2009; Yver et al., 2009), with winter H<sub>2</sub>/CO ratios somewhat lower compared to summer ratios, a careful detailed analysis is beyond the scope of this paper. In a similar manner, the low diesel exhaust H<sub>2</sub>/CO ratio of <0.2

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has a “diluting” effect on the overall gasoline-dominated ratio. However, because the absolute H<sub>2</sub> and CO emissions from a diesel engine are much smaller than those from a gasoline engine, it would require a very large diesel fraction of a vehicle fleet to significantly affect the gasoline-dominated ratio.

It remains to be investigated to what extent our findings of negligible H<sub>2</sub> emissions from oil and gas burners are applicable for similar burner/heater systems in other parts of the world. Our results suggest that the heater system (oil vs. natural gas) or the age and design are not of prime relevance, but mainly how well the burner is tuned. As for the low H<sub>2</sub> emissions from our sampled waste incinerator plants, these results are unlikely applicable to less controlled incineration of waste, particularly in landfills. Our analysis also reveals the lack of knowledge on H<sub>2</sub> emissions from coal combustion, which could potentially be a significant fossil fuel combustion source of H<sub>2</sub>. This may be one explanation for our estimated fossil fuel H<sub>2</sub> emissions being considerably smaller compared to those by e.g. Yver et al. (2011) and Ehhalt and Rohrer (2009).

Our surprising findings of a lack of H<sub>2</sub> emissions in the presence of CO emissions, and the isotopic hydrogen signatures of these exhausts suggest that our understanding of the H<sub>2</sub> and CO involvement in these combustion processes is incomplete. More studies involving quantification of H<sub>2</sub>O, along with isotope analysis on the main H and C-containing compounds may help in this process. Combustion experiments with controlled (including zero) H<sub>2</sub> mole fractions and isotope signatures in the advected air could help to better understand the exhaust H<sub>2</sub> characteristics of fossil fuel burner systems with low emissions.

**Supplementary material related to this article is available online at:**

**<http://www.atmos-chem-phys-discuss.net/12/6839/2012/>**

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**Table 1.** Global sinks and sources of tropospheric molecular hydrogen (H<sub>2</sub>) and their isotope signatures<sup>a</sup>.

	Strength <sup>b</sup> [Tgyr <sup>-1</sup> ]	isotope signature [‰ VSMOW <sup>d</sup> ]	
Sources	Fossil fuel combustion	11–20	–196 <sup>e</sup> to –270 <sup>f</sup>
	Biomass and biofuel burning	8 <sup>c</sup> –20	–90 <sup>g</sup> to –290 ± 60 <sup>e</sup>
	Photochemical production	25–44	130 to 340 <sup>h</sup>
	from methane	15–26	190 ± 50 <sup>i</sup> to 213 <sup>+264</sup> <sub>-228</sub>
	from VOC	10–18	–
	Land N <sub>2</sub> fixation	0–6	–700 <sup>l</sup>
Oceanic N <sub>2</sub> fixation	3–6	–628 <sup>k</sup> to –700 <sup>l</sup>	
Total Sources	47–96		
Sinks			kinetic isotope fractionation factors
	Soil deposition	55–88	0.943 ± 0.024 <sup>e</sup>
	Reaction with OH	15–19	0.568 <sup>m</sup>
Total Sinks	70–107		

<sup>a</sup>: these estimates result in a tropospheric H<sub>2</sub> burden of 136–172 Tg, a mean isotopic composition of 120–132, and a tropospheric lifetime of 1.4–2 yr.

<sup>b</sup>: ranges from the works of Novelli et al. (1999); Hauglustaine and Ehhalt (2002); Sanderson et al. (2003); Rhee et al. (2006b); Price et al. (2007); Xiao et al. (2007); Ehhalt and Rohrer (2009); and Pieterse et al. (2011).

<sup>c</sup>: lower value from this work for the year 2000.

<sup>d</sup>: referenced to Vienna Standard Mean Ocean Water (VSMOW).

<sup>e</sup>: from Gerst and Quay (2001).

<sup>f</sup>: from Rahn et al. (2002b).

<sup>g</sup>: from Rhee et al. (2006b).

<sup>h</sup>: range from works of Gerst and Quay (2001), Rahn et al. (2003), Röckmann et al. (2003), Rhee et al. (2006b), Price et al. (2007), and Mar et al. (2007).

<sup>i</sup>: from Rhee et al. (2006a).

<sup>k</sup>: Rice and Quay, unpublished results.

<sup>l</sup>: from Walter et al. (2011)

<sup>m</sup>: from Sander et al. (2006) based on Ehhalt et al. (1989) and Talukdar et al. (1996).

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**Table 2.** Molecular hydrogen ( $\text{H}_2$ ), its isotopic composition ( $\delta\text{D}$ ), carbon monoxide (CO), carbon dioxide ( $\text{CO}_2$ ), and methane ( $\text{CH}_4$ ) in the exhausts of oil (O), gas (G) and wood (W) heaters, waste incinerators (I), and from ambient air samples (A). The incinerator samples are from 7 different incinerators (some measurement campaigns were repeated, hence 9 sets listed) and collected using discrete flask/bag or integrated (1 day or 1 week) samples. S-Air and I-Air samples are ambient air samples collected during the study. Mole fractions (dry air) are given in ppm ( $10^{-6}$ ) for  $\text{H}_2$ , CO, and  $\text{CH}_4$ , and in percent ( $10^{-2}$ ) for  $\text{CO}_2$ . For  $\delta\text{D}$ , see text.

Sample	Type	$\text{H}_2$ [ppm]	$\delta\text{D}$ [‰]	CO [ppm]	$\text{CO}_2$ [%]	$\text{CH}_4$ [ppm]
S-1A	O	0.527	-25.6	10.7	6.33	1.17
S-1B	O	0.455	-34.7	7.01	6.10	1.20
S-2A	O	0.204	-52.3	4.59	10.2	0.54
S-2B	O	0.187	-139	3.70	10.2	0.54
S-3A	G	0.403	-22.3	2.42	4.60	1.04
S-3B	G	0.397	-17.8	2.37	4.47	1.05
S-4A	G	0.389	63.7	0.95	2.95	1.48
S-4B	G	0.638	30.9	3.04	0.15	20.1
S-5A	G	0.222	-206	15.4	8.89	0.19
S-5B	G	0.582	25.0	0.44	0.18	22.1
S-6A	G	0.413	-103	2.43	10.6	0.00
S-6B	G	0.460	-108	2.47	10.6	0.03
S-7A	G	3.36	-169	25.6	9.23	37.6
S-7B	G	3.39	-167	25.5	8.85	43.1
S-8A	W	20.6	-47.9	583	7.31	5.19
S-8B	W	6.65	-182	69.5	8.74	1.26
S-9A	W	120	-204	699	2.92	49.2
S-9B	W	381	-87.2	4090	3.35	102
S-Air	A	0.551	55.9	0.32	0.05	1.99

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**Table 2.** Continued.

Sample	Type	H <sub>2</sub> [ppm]	δD [‰]	CO [ppm]	CO <sub>2</sub> [%]	CH <sub>4</sub> [ppm]
I-1A	I	0.383	-229	7.54	8.80	-
I-1B	I	0.344	-308	7.54	8.80	-
I-1C	I	0.367	-	5.03	9.60	-
I-1D	I	0.616	-357	4.05	9.70	-
I-1E	I	0.341	-	-	-	-
I-2A	I	1.99	-173	30.6	9.40	-
I-2B	I	2.11	-165	30.6	9.40	-
I-2C	I	2.35	-	32.0	9.60	-
I-2D	I	2.05	-192	32.0	9.60	-
I-2E	I	1.92	-	31.1	9.60	-
I-2F	I	2.20	-157	31.1	9.60	-
I-3A	I	0.591	-	5.81	9.99	0.40
I-4A	I	4.71	-	9.97	9.51	1.20
I-4B	I	0.250	-	3.08	9.57	<0.40
I-4C	I	0.270	-	3.39	9.72	<0.40
I-5A	I	3.450	-	3.35	9.80	<0.40
I-5B	I	4.720	-	9.14	9.42	1.16
I-6A	I	0.863	-	11.4	9.87	<0.40
I-6B	I	0.668	-	11.6	9.70	<0.40
I-6C	I	0.726	-	12.8	10.2	<0.40
I-7A	I	0.265	-	5.55	9.59	<0.40
I-7B	I	0.375	-	3.78	9.19	<0.40
I-7C	I	0.268	-	3.95	9.49	<0.40
I-8A	I	0.677	-	6.72	10.3	<0.40
I-8B	I	0.742	-	6.45	10.2	<0.40
I-8C	I	4.75	-	11.1	10.4	0.76
I-9A	I	0.593	-	8.14	10.1	0.47
I-9B	I	0.574	-	7.41	10.0	0.43
I-9C	I	0.618	-	6.28	9.93	<0.40
I-Air1	A	0.499	88.0	0.20	-	<0.40
I-Air2	A	0.529	19.6	0.18	-	<0.40

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**Table 3.** Molar [ $\text{ppm ppm}^{-1}$ ] ratios of molecular hydrogen ( $\text{H}_2$ ) to carbon monoxide ( $\text{CO}$ ), to methane ( $\text{CH}_4$ ), and isotopic signatures ( $\delta\text{D-H}_2$ ) for selected combustion processes. Global  $\text{H}_2$  emissions (in Tg) are given for 2000, 2005, and 2010. See Supplement for more data on biofuel and biomass burning.

	absolute $\text{H}_2/\text{CO}$	relative <sup>a</sup> $\Delta\text{H}_2/\Delta\text{CO}$	absolute $\text{H}_2/\text{CH}_4$	relative <sup>a</sup> $\Delta\text{H}_2/\Delta\text{CH}_4$	$\delta\text{D-H}_2$ [‰ VSMOW]	Global Emissions		
						2000	2005	2010
transportation								
gasoline, road	0.5 <sup>b</sup>	0.5 <sup>b</sup>	–	–	$-270 \pm 50^{\text{d}}$	$8.2 \pm 2.1$	$5.9 \pm 1.5$	$3.8 \pm 0.94$
diesel, road	$0.15 \pm 0.1$	$<0.15 \pm 0.1$	–	–	–	$0.43 \pm 0.31$	$0.38 \pm 0.27$	$0.32 \pm 0.23$
diesel, rail & water	$0.15 \pm 0.1$	$<0.15 \pm 0.1$	–	–	–	$0.43 \pm 0.31$	$0.38 \pm 0.27$	$0.32 \pm 0.23$
waste incinerators	0.05–0.1	0	$2 \pm 1$	$<0$	$-250 \pm 100$	neg <sup>g</sup>	neg <sup>g</sup>	neg <sup>g</sup>
residential (domestic)								
oil and gas heaters	0.01–0.1	0	var <sup>f</sup>	var <sup>f</sup>	$-100 \pm 50$	neg <sup>g</sup>	neg <sup>g</sup>	neg <sup>g</sup>
biofuel	$0.25 \pm 0.05^{\text{c}}$	$0.25 \pm 0.05^{\text{c}}$	$3.3^{\text{c}}$	$3.3^{\text{c}}$	$-290 \pm 60^{\text{e}}$	$2.7 \pm 0.7^{\text{h}}$	$2.8 \pm 0.7^{\text{h}}$	$3.0 \pm 0.8^{\text{h}}$
biomass	$0.25 \pm 0.05^{\text{c}}$	$0.25 \pm 0.05^{\text{c}}$	$3.3^{\text{c}}$	$3.3^{\text{c}}$	$-290 \pm 60^{\text{e}}$	$5.7 \pm 1.4^{\text{i}}$	$8.4 \pm 2.1^{\text{i}}$	$9.4 \pm 2.3^{\text{i}}$

<sup>a</sup>: ratio after subtraction of background mole fractions.

<sup>b</sup>: based on works by Vollmer et al. (2007); Hammer et al. (2009).

<sup>c</sup>: based on works by Cofer III et al. (1989, 1990, 1996); Laursen et al. (1992) and supported by this study.

<sup>d</sup>: based on Rahn et al. (2002b) with uncertainty based on rough estimate using results by Vollmer et al. (2010).

<sup>e</sup>: Gerst and Quay (2001).

<sup>f</sup>: highly variable.

<sup>g</sup>: negligible compared to other  $\text{H}_2$  combustion sources.

<sup>h</sup>: based on EDGARv4.2 with the value for 2010 extrapolated from earlier years.

<sup>i</sup>: GFED3 (Giglio et al., 2010; Van der Werf et al., 2010) with considerable inter-annual variability in the full 1997–2010 record.

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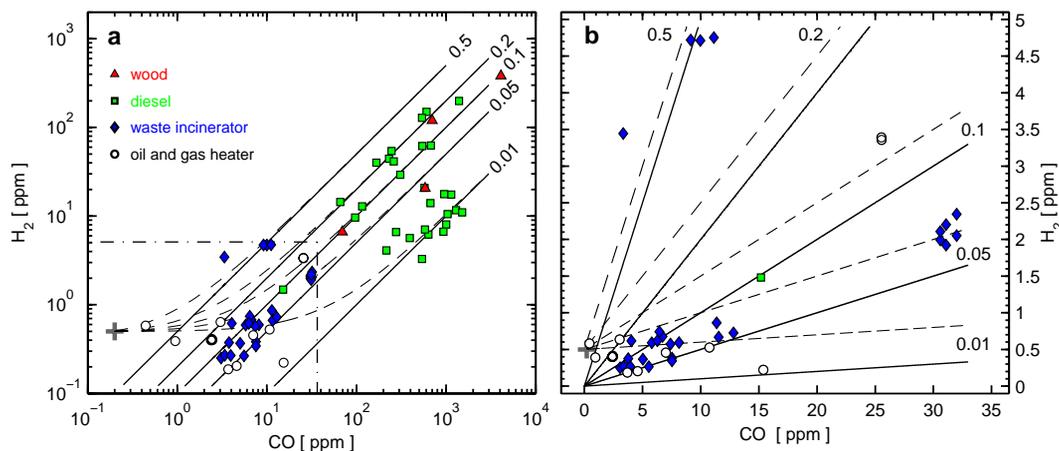
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## Molecular hydrogen from residential combustion

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**Fig. 1.** Molecular hydrogen ( $\text{H}_2$ ) versus carbon monoxide (CO) in combustion exhaust. The measurements are shown on a log-log scale in (a) and a selection (delimited by dashed-dotted box) in (b). The  $\text{H}_2$  and CO mole fractions in background air are shown as grey plus sign. Molar  $\text{H}_2/\text{CO}$  ratio lines are shown as visual guides with the origins set at background mole fractions ( $\Delta$  ratio, see text) shown as dashed lines and at zero mole fractions (absolute ratios) as solid lines.

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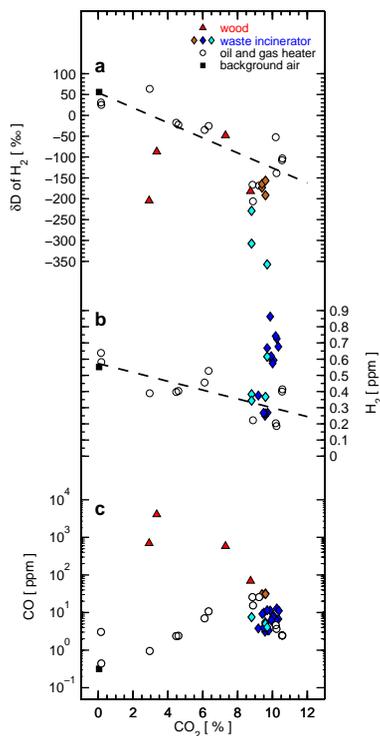
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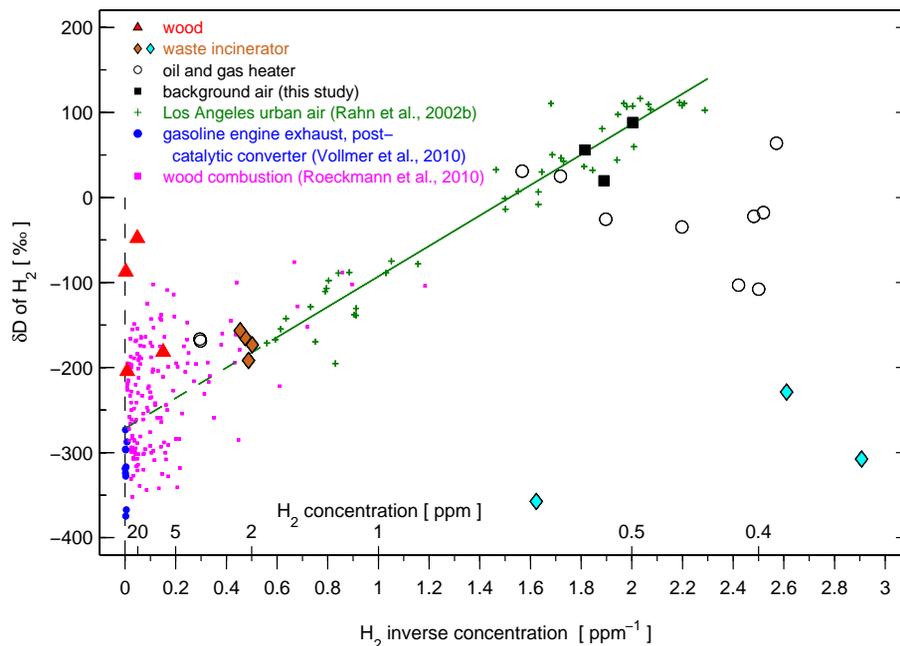


**Fig. 2.** Molecular hydrogen ( $H_2$ ) isotopic composition ( $\delta D$ , panel **a**),  $H_2$  (panel **b**) and carbon monoxide (CO, panel **c**) mole fractions versus carbon dioxide ( $CO_2$ ) from residential heating combustion and waste incinerator plants. Not all waste incinerator measurements appear in all three subplots because they were either not measured or exceeded the plotting range. Cyan diamonds are for waste incinerator I-1, those in orange are for I-2, and those in dark blue are from a later measurement campaign when no isotope measurements were conducted (I-3 to I-9). Samples with  $H_2$  mole fractions  $>1$  ppm (I-2) are omitted from (**b**). The dashed lines are linear fits through the oil and gas heater measurements, excluding S-7.

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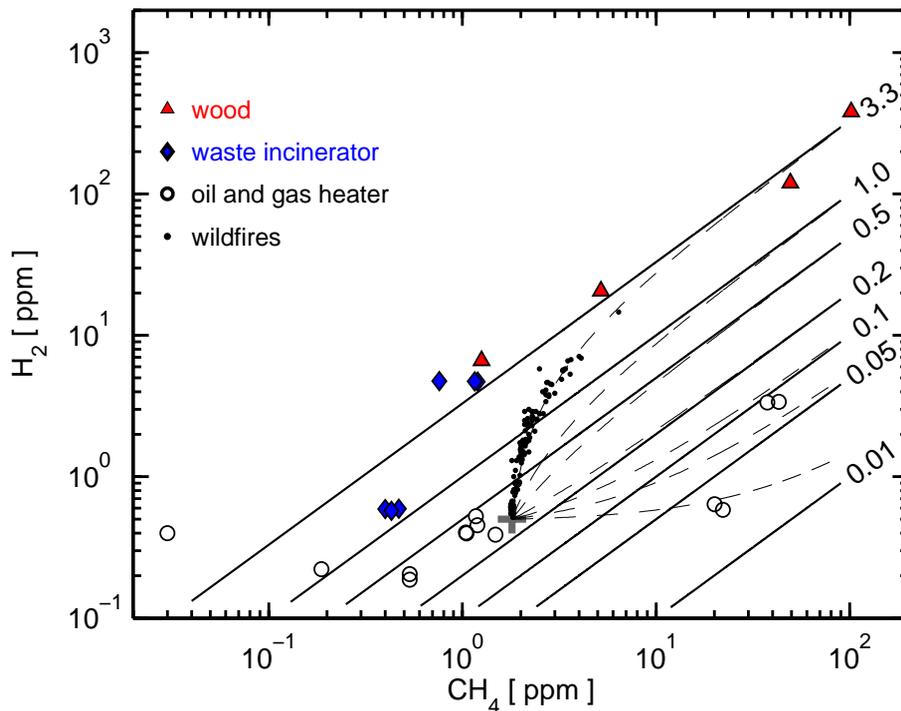

## Molecular hydrogen from residential combustion

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**Fig. 3.** Relationship of molecular hydrogen ( $H_2$ ) isotopic composition ( $\delta D$ ) versus inverse  $H_2$  mole fraction (“Keeling plot”) for samples from this study compared with results from Rahn et al. (2002a) with a green line fitted through their data, from Vollmer et al. (2010), and Röckmann et al. (2010a). Some of our samples are in fair agreement with the relationship found by Rahn et al. (2002a): these are the poorly-adjusted natural gas combustion burners from one waste incinerator plant (using natural gas post-filter combustion for  $NO_2$  removal) and one residential heater. Most oil and gas heater and waste incinerator samples show an opposite relationship, i.e. decreasing mole fraction for decreasing  $\delta D$ .

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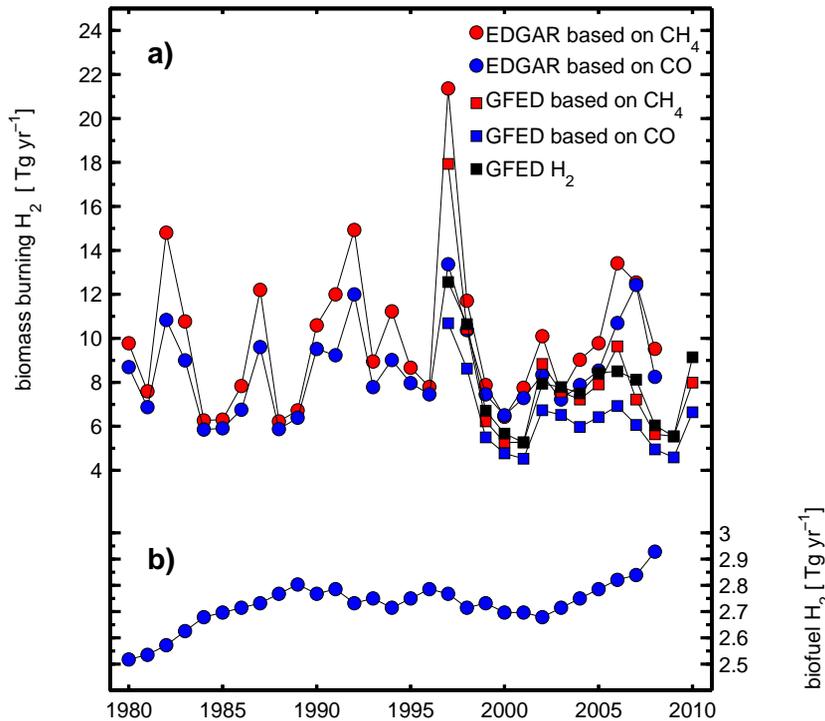
**Fig. 4.** Molecular hydrogen ( $H_2$ ) versus methane ( $CH_4$ ) in combustion exhaust. The measurements are shown on a log-log scale. Results from wildfires are from Cofer III et al. (1989, 1990, 1996). The  $H_2$  and  $CH_4$  mole fractions in background air are shown as grey plus sign. Molar  $H_2/CH_4$  ratio lines are shown as visual guides with the origins set at background mole fractions ( $\Delta$  ratio, see text) shown as dashed lines and at zero mole fractions (absolute ratios) as solid lines.

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**Fig. 5.** Global molecular hydrogen ( $H_2$ ) emissions from biomass burning (a) and domestic emissions (b, with finer y-axis resolution) using emission inventories from the Emission Database For Global Atmospheric Research (EDGARv4.2) project (Olivier et al., 2002), and the Global Fire Emissions Database version 3 (GFED3, data set at <http://www.globalfiredata.org/>, see also Giglio et al. (2010) and Van der Werf et al. (2010)). The carbon monoxide (CO) emission inventories were converted to  $H_2$  using a molar  $H_2/CO$  ratio of 0.25, and the methane ( $CH_4$ ) emission inventories were converted to  $H_2$  using a molar  $H_2/CH_4$  ratio of 3.3 (see text). GFED3  $H_2$  and  $CH_4$ -derived  $H_2$  emissions agree well, while CO-derived  $H_2$  emissions are considerably lower. EDGAR emissions are generally larger than GFED3 emissions.